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<p>A summary is presented of research carried out over the three year period October 1, 1984 — September 30, 1987 on the program "Synthetic Metals from Intercalated Graphite". The research covers Synthesis and Compositional Characterization of Graphite Intercalation Compounds, Structural Studies, Lattice Mode Studies, Electronic Structure, Transport Properties, Magnetic Studies in Graphite Intercalation Compounds, Superconductivity Studies in Graphite Intercalation Compounds, and Review Articles and Plenary Invited Talks.</p>					
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**Final Report
to the
Air Force Office of Scientific Research
for research on
Synthetic Metals from Intercalated Graphite**

**AFOSR Contract #F49620-83-C-0011
for the period
October 1, 1984 — September 30, 1987**

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1 Overview

1.1 Abstract of Objectives

During the three year period October 1, 1984—September 30, 1987, efforts on the Program "Synthetic Metals from Intercalated Graphite" were largely focused on studies of magnetic and superconducting graphite intercalation compounds. We review in this report the progress that was made, referring to the publications that were prepared on each of the topics under investigation.

1.2 Statement of Work

Statement of work in AFOSR contract #F49620-83-C-0011 on "Synthetic Metals from Intercalated Graphite".

- Derive techniques for improved methods for the preparation and characterization of specific graphite intercalation compounds.
- Synthesize new intercalated systems and study their structure.
- Study in-plane structure and phase transitions in the intercalate layers with electron diffraction, lattice fringing, real space electron microscope imaging, and high resolution x-ray scattering.
- Deduce structural phase diagrams for specific graphite intercalation compounds.
- Investigate in detail commensurate-incommensurate phase transitions.
- Study lattice modes by infrared and Raman spectroscopy, and inelastic neutron scattering.
- Derive models for the phonon dispersion relations throughout the Brillouin zone, and apply these models to interpret lattice mode studies.
- Model the electronic dispersion relations and apply these models to interpret the experimental results relevant to the electronic properties.
- Measure and model thermal transport phenomena in intercalated graphite.
- Measure the temperature and field dependence of the magnetic susceptibility and heat capacity of magnetic graphite intercalation compounds and to construct magnetic phase diagrams for these systems.
- Study the superconductivity of specific graphite intercalation compounds.

2 Three Year Summary of Research Effort

A summary of the status of the research effort on "Synthetic Metals from Intercalated Graphite" is presented in terms of the progress made during the period October 1, 1984 to September 30, 1987. In presenting the summary, we refer by number (#n) to the publications listed in the Publications section (3.1).

2.1 Synthesis and Compositional Characterization of Graphite Intercalation Compounds

2.1.1 A New Method for Synthesis of Potassium-Hydrogen Graphite Intercalation Compounds

A new method for the synthesis of potassium-hydrogen graphite intercalation compounds, based on the direct intercalation of KH (# 28) was extended to synthesize the corresponding compounds with deuterium. The method has also yielded a well-staged KH-GIC sample of high stage (stage 4). The KH-GIC samples have been characterized for staging homogeneity by (00 ℓ) x-ray diffraction and for in-plane structure by transmission electron microscopy (TEM) (# 27). Raman microprobe studies have given information about staging homogeneity (# 27, # 40).

2.1.2 Implantation-Enhanced Intercalation

We have shown that if a graphite sample is first ion implanted, then the ability to intercalate certain species is greatly enhanced. This concept has been applied to enhance the intercalation of sodium, which does not readily intercalate graphite (# 7, # 13). Since the implantation of carbon and argon into graphite also enhances the subsequent intercalation of sodium, we conclude that implantation-enhanced intercalation is due to a defect mechanism rather than to a catalytic process. An extension of the implantation-enhanced intercalation concept was used to introduce Fe into graphite (# 86), since Fe cannot be intercalated directly. In this work much lattice damage was introduced. The study of enhanced sodium intercalation was the topic of the M.S. thesis of H. Menjo.

2.1.3 Use of Rutherford Backscattering for the Characterization of Graphite Intercalation Compounds

The Rutherford backscattering (RBS) technique has been applied to provide unique information on the structure of GICs. Conventional RBS studies have yielded information on the depth distribution of the chemical constituents (# 17) in both air-stable and reactive GICs. With the RBS channeling spectra, unique information has been obtained with regard to interplanar alignment and the effect of structural phase transitions on this alignment. The Rutherford backscattering experiments were carried out at Bell Laboratories in collaboration with Drs. T. Venkatesan and B. Wilkens.

2.2 Structural Studies

2.2.1 High Resolution Structural Studies Using Electron Microscopy

High resolution Transmission Electron Microscopy (TEM) studies have been carried out on well staged SbCl_5 -GIC (# 16, # 25, # 39, # 49) samples and KH-GIC (# 19, # 27, # 40, # 48) samples based on both single crystal "kish" graphite and highly oriented pyrolytic graphite (HOPG) host materials. For the SbCl_5 -GIC system, a transition from a commensurate intercalate phase at room temperature to a glassy phase is readily observed below $\sim 150\text{K}$ (# 49) using transmission electron microscopy techniques. This phase transition is very unusual insofar as the low temperature phase is the glassy phase. High resolution x-ray studies were carried out to identify this transition more fully, but no such transition could be observed with x-ray scattering using both kish and vermicular graphite host materials. Detailed TEM results show that the glassy phase is induced by the electron beam irradiation through a radiolysis mechanism. The dependence of the critical electron dose necessary to induce the glass phase has been determined as a function of electron beam energy and sample temperature. The activation energy for the formation of the glass phase changes dramatically from $\sim 0.11\text{ eV}$ above $\sim 150\text{ K}$ to $\sim 0.01\text{ eV}$ below $\sim 150\text{ K}$. Models for the structure of SbCl_5 - GIC are suggested using computer image simulations of high resolution lattice images as a function of transmission electron microscope parameters, e.g., defocus.

For the KH-GICs, lattice fringe imaging techniques have been used to obtain unique information about the c-axis structure on an atomic level (# 19, # 27, # 38). In addition to the c-axis repeat distances observed in (00ℓ) x-ray diffraction, a variety of other structures are observed. Some structures are related to hydrogen-deficient regions separating KH-GIC regions from K-GIC regions, and other structures related to a periodic arrangement of KH and K heterostructure superlattices. Unique information on the in-plane structure has likewise been obtained, showing the (2×2) structure to be dominant for samples prepared at high temperature (e.g., 490°C) and the $(\sqrt{3} \times \sqrt{3})$ structure dominant for samples prepared at lower temperatures (e.g., 260°C). In a complementary (00ℓ) x-ray study (# 27), the kinetics of the formation of the KH compounds has been investigated. The results show that with the direct KH intercalation method, a stage n K-GIC is rapidly formed, and subsequently over a relatively long time additional K and H species are intercalated to form the final KH compound of stage n , where $n = 1, 2$. This kinetic process was independently found by Guérard and coworkers in France.

2.2.2 High Resolution Microscopy Studies of MnCl_2 -GICs

An in-depth high resolution transmission electron microscopy (TEM) study of magnetic GICs was carried out since 1985 by Jim Speck, who is working on this problem in collaboration with Dr. J.M. Gibson at AT&T Bell Labs. Because of the availability of good stage 1 MnCl_2 -GIC samples from our synthesis program, most of the high resolution measurements were made on this material. Particular emphasis has been

given to determining the relation of the incommensurate intercalate structure to that of the adjacent graphite layers. A second focus of the work has been directed to the structure and temperature dependence of the intercalate islands (# 61, # 62, # 69).

In-plane electron diffraction patterns from stage 1 MnCl_2 -GICs typically show an $R(30 - \alpha)^\circ$ phase (# 61), where $0 < \alpha < 4$ (this notation represents the rotation angle between the in-plane carbon crystal axis and the metal chloride crystal axis). This structure is different in detail from that for the stage 1 CoCl_2 -GICs. Four valuable pieces of information are obtained from the diffraction pattern. (1) The in-plane lattice parameters in the metal chloride sandwich are within 1% of the values in the pristine material. (2) The intercalant sandwich is translationally incommensurate with respect to the carbon lattice, but it is orientationally locked to the carbon. (3) Qualitative kinematical intensity calculations show that the chloride layer has $\bar{3}$ symmetry which is identical to the close packed layer in the pristine MnCl_2 . (4) Careful examination of the intercalant reflections reveals a clustering of reflections within an angular spread of $\sim 4^\circ$, but all for the same intercalant lattice constants. This slight orientational rotation between chloride layers leads to Moiré fringe images in dark field TEM images.

2.2.3 High Resolution X-Ray Scattering Studies

To explain the unusual low temperature glass phase in SbCl_5 -GICs, high resolution x-ray studies were carried out from 14 K to 300 K in search of the glass phase (# 16, # 39, # 49). To determine whether sample thickness could be related to the observation of a glass phase, experiments were carried out using both kish and vermicular graphite host materials. The failure to observe the glass phase in high resolution x-ray experiments under a wide variety of conditions provided an essential step in the identification of the glass phase formation with an electron beam irradiation mechanism.

In previous work, we identified for the first time a stripe domain phase transition in the bromine-GIC system at elevated temperature, predicted theoretically in 1949. We have now identified a new novel commensurate-incommensurate phase transition in the same system at low temperature (# 55).

A detailed structural study is underway on the phase transitions in KHg -GICs which exhibit unusual anisotropic superconductivity at low temperatures. One objective is to understand the structural effect of hydrogen uptake, which strongly accentuates the superconducting behavior. A second objective is to determine whether the trilayer ordering of an intercalate sandwich is maintained upon intercalate melting (# 85).

2.2.4 Model for Staging in Intercalated Graphite

A model for staging has been developed (# 21) based on an evaluation of the partition function for attractive in-plane and repulsive interplanar interactions. Mixed staging is found at high temperatures below the disordering temperature. This study was carried

out in collaboration with the late Professor David Adler and his graduate student J.C. Schön.

2.3 Lattice Mode Studies

2.3.1 Raman Microprobe Studies

A Raman microprobe has been set up for particular application to the study of the Raman spectra in ordered and disordered graphites and graphite intercalation compounds (# 3, # 11). The availability of this new instrument has enabled us to use our knowledge of the phonon dispersion relations of GICs to characterize the spatial homogeneity of the staging in GIC samples to $\sim 2\mu\text{m}$ resolution.

2.3.2 Raman Characterization of Potassium-Hydrogen Intercalated Graphite

The Raman shifts of the E_{2g_2} modes in KH-GICs were determined and compared with binary K-GICs and ternary KHg-GICs (# 18, # 40). The strong electron affinity of hydrogen plays an important role in shifting the E_{2g_2} mode of stage-1 KH-GICs to higher wavenumbers than for the stage-1 alkali-metal GICs. Of particular interest also is the drastic change in lineshape from that for the stage 1 K-GIC which shows a strong Breit-Wigner lineshape to that for the stage 1 KH-GIC which is Lorentzian, consistent with a large reduction in the graphite-intercalate layer coupling as electrons are transferred to the hydrogen from the potassium and graphite π -bands.

2.4 Electronic Structure

2.4.1 Charge Transfer Mechanism in Acceptor-GICs

Fundamental differences between the charge transfer mechanism in acceptor and donor compounds are identified (# 34). A new band structure mechanism is proposed for charge transfer in an acceptor compound, valid for molecular acceptor compounds (such as Br_2 -GICs) which exhibit a commensurate intercalate layer with long range in-plane coherence. For acceptor compounds such as the Br_2 -GICs, defect mechanisms such as disproportionation and intercalate island structures cannot account for charge transfer.

2.4.2 Occupation of Intercalate Bands in Stage 1 Alkali Metal-GICs

A review was prepared of the experimental evidence relevant to the occupation of the intercalate bands in the stage 1 alkali metal compounds C_8K , C_8Rb , and C_8Cs (# 10), a point of current controversy. Neither the experimental nor the theoretical evidence is conclusive on this point. Various experiments to clarify this important point are suggested.

2.4.3 Charge Transfer in the Stage 1 Alkali Metal-GICs

There has been a good deal of controversy concerning charge transfer in the stage 1 alkali metal-GICs, in particular whether or not the charge transfer from the alkali metal to the graphite is complete for the heavy alkali metals K, Rb, and Cs. An analysis of ESR linewidth measurements for C_8K and C_8Rb has been carried out, giving evidence for occupation of Γ -point bands, indicative of incomplete charge transfer by the alkali metal. The calculations show a considerable amount of s-character admixture with levels near the Fermi surface. The spin-lattice relaxation rate associated with the ESR line width ΔH in the first stage alkali metal GICs has been calculated. We conclude that the direct Elliot mechanism is too small to account for the observed ΔH above 100K, where ΔH is proportional to T . An interplay between the graphitic electron spin- Γ -band spin exchange interaction and the Elliot mechanism for the Γ -band spin provides a qualitative explanation for the observed results. Our results indicate that the Γ -point band minimum lies below the Fermi level E_F (# 66).

2.4.4 Shubnikov-de Haas Effect in the KH-GIC System

Results on the Fermi surface for KH-GICs have been obtained using the Shubnikov-de Haas effect (# 27, # 28, # 40, # 50, # 53). Characteristic Shubnikov-de Haas frequencies have been observed for stage 1, 2 and 4 KH-GICs. Each of the spectra have been analyzed in terms of the rigid band model, but it is only for stage 4 that good agreement is obtained with the model, as would be expected since stage 1 and stage 2 should not be well described by the dilute limit model. The interpretation of the Shubnikov-de Haas results assumes full occupation of the hydrogen levels, consistent with the strong electron affinity of hydrogen.

2.5 Transport Properties

2.5.1 C-Axis Conductivity in GICs

The very large anisotropy and unusual stage dependence has recently been observed experimentally in both donor and acceptor compounds. This effect has been modeled (# 88) using two mechanisms. The interaction of the carriers with the LO-phonons polarized along the c-axis is most important in the low stage compounds with large charge transfer, whereas the scattering of carriers by stacking faults is the dominant mechanism for the high stage compounds.

2.5.2 High Field Magnetoresistance Anomaly in Graphite

The role of impurities and charge imbalance in the high field magnetoresistance anomaly in graphite was studied and modeled (# 4), showing that the detailed behavior at the magnetoresistance anomaly is highly sensitive to the concentration of charged impurities, which give rise to the breaking of pair states. By measuring the magnetoresistance

with pulsed currents, it was shown that the magnitude of the anomaly exhibits a non-linear dependence on the electric field (# 6, # 12, # 22). In this work it was also established that the charge density wave occurs in the basal plane (# 12, # 46) and not along the c-axis as had been proposed by Yoshioka and Fukuyama. A detailed experimental determination down to ~ 0.3 K of the field dependence of the transition temperature showed deviations from the theoretical prediction (# 12).

2.5.3 Magnetic Phase Transitions in C_6Eu observed by High Field Magnetoresistance

The magnetic phase transitions in the donor compound C_6Eu , previously observed in the magnetization by Suematsu et al., have been verified in high field magnetoresistance measurements, including transitions from a triangular planar spin arrangement to a ferrimagnetic spin arrangement, to a canted spin phase, to a ferromagnetic phase (# 36, # 43, # 52, # 56). The high field magnetoresistance measurements clearly show an additional canted spin phase. Monte Carlo spin simulation calculations have been used to identify the magnetic phases (# 52). A model based on magnon drag effects has been developed to account for the resistivity changes at the magnetic phase transition (# 44).

2.5.4 Thermal Expansion Coefficient of $SbCl_5$ -GICs

The thermal expansion coefficient was measured up to room temperature and a model was developed to explain the observed temperature dependence, taking into account the expansion within the constituent layers of a unit cell (# 47).

2.5.5 Low Temperature Thermoelectric Power Anomalies in Graphite

A new type of anomaly in the thermoelectric power of graphite at low temperature has been identified and a model based on phonon drag effect has been developed to explain the observed phenomena (# 60).

2.5.6 Ideal Resistivity in Graphite Intercalation Compounds

High resolution low temperature resistivity measurement were carried out, showing that the resistivity is well represented by the functional form

$$\rho(T) = A + BT + CT^2$$

down to the lowest temperature in contrast to the behavior of conventional metals which show an approximate T^5 dependence (# 51).

2.6 Magnetic Studies in Graphite Intercalation Compounds

2.6.1 Zero Field Susceptibility of Finite Size Kosterlitz-Thouless Systems

To explain the experimental susceptibility measurements in CoCl_2 -GICs, finite size effects have been considered from a theoretical point of view (# 2, # 5, # 32, # 33, # 57). In particular, finite size effects in the Kosterlitz-Thouless transition have been investigated using the renormalized spin wave-vortex gas method. By imposing an upper limit on the length scale and a lower limit for the spin wave integral, the finite size rounding of the susceptibility in the 2D-XY model is obtained. The differential magnetic susceptibility is calculated numerically by integrating the spin-spin correlation function and the result is normalized to the high temperature series expansion for the classical 2D-XY model. Application of this theory has been made to the CoCl_2 -intercalated graphite system.

2.6.2 Competing Field Induced Transitions in the Two-Dimensional XY Model

In studying the magnetic properties of CoCl_2 -GICs, two symmetry breaking fields are present: the in-plane 6-fold crystal field and the external magnetic field. In this connection the ferromagnetic two-dimensional XY model with a p -fold symmetry-breaking field H_p , subjected to an in-plane external field H applied at an angle ω ($0 \leq \omega \leq \pi/p$) with respect to the p -fold axis, has been analyzed exactly at zero temperature. (# 23, # 24). A spin-flip type transition occurs at a critical field $H_C = p^2 H_p$ and at a critical angle $\omega_0 = \pi/p$. At this critical point, the parallel differential susceptibility, χ_{\parallel} , (where the probing field h_{\parallel} is parallel to H), jumps discontinuously to zero and the perpendicular differential susceptibility, χ_{\perp} , (where the probing field h_{\perp} is perpendicular to H), diverges like $(H_C - H)^{1/2}$. A self consistent harmonic approximation is applied for the low temperature analysis and numerical results for the magnetization, the parallel susceptibility and the perpendicular susceptibility are obtained. The singularities of the zero temperature analysis are retained when random averages are taken numerically over the angle ω for the parallel susceptibility and magnetization. These concepts have been applied to measurements of the magnetic properties of two-dimensional systems.

More recently, Monte Carlo simulations have been carried out of the magnetic phase transitions in CoCl_2 -GICs at low temperatures (# 64, # 72).

2.6.3 Temperature Dependence of the Magnetic Susceptibility of CoCl_2 -GICs

Previously measured differential magnetic susceptibility data for stage 1, 2 and 3 CoCl_2 -GIC samples have been analyzed using the high temperature expansion expansion of the classical spin model in two dimensions, yielding conclusive evidence for a classical 2D-XY model description of the magnetic properties of CoCl_2 -GICs (# 32, # 33). Deviations from the high temperature expansion analysis have been

studied using the theory of the finite size Kosterlitz-Thouless transition, with size as an adjustable parameter. The effect of the symmetry breaking field has been analyzed using a generalized Jose-Kadanoff-Kirkpatrick-Nelson (JKKN) model. A qualitative understanding of the susceptibility anomalies in CoCl_2 -GICs is achieved. It is found that the CoCl_2 -GICs are approximately a classical 2D-XY system with a ferromagnetic exchange coupling $J_{eff} = 7.125 \text{ K}$. A Kosterlitz-Thouless transition takes place at $T \approx 10 \text{ K}$ and the divergent susceptibility is rounded off by finite size effects as well as the effects of the probing field. The initial decrease in the susceptibility for $T \leq 10 \text{ K}$ is a result of the in-plane 6-fold symmetry breaking field. The low temperature phase is consistent with the picture of ferromagnetic layers of XY spins coupled antiferromagnetically. The model Hamiltonian that describes the magnetic properties of CoCl_2 -GICs is given by four terms (# 8, # 9). The dominant term is the classical 2D-XY Hamiltonian. The perturbations consist of a 1-fold symmetry-breaking field with Zeeman coupling to the external field, a six-fold symmetry-breaking field corresponding to the phenomenological six-fold in-plane anisotropy, and an antiferromagnetic inter-planar coupling. This magnetic Hamiltonian is used to interpret the experimental susceptibility and magnetization for CoCl_2 -GICs (# 5, # 14).

2.6.4 Two-Dimensional Spin-Flop Transition in CoCl_2 -GICs

Field-induced susceptibility anomalies are observed in the quasi two-dimensional spin system of CoCl_2 -intercalated graphite (# 20, # 42, # 57, # 58). These anomalies are explained using the Landau free energy functional applied to the magnetic Hamiltonian of CoCl_2 -intercalated graphite. The low field anomaly is identified with a two-dimensional antiferromagnetic-spin-flop first-order transition. The higher field anomaly is identified with a spin-flop-ferromagnetic second-order transition. The low temperature properties of these three phases in the stage 1 CoCl_2 -GIC have been analyzed using the transfer matrix method for their c -axis ordering. A comparison of the theory with experimental data has been made. Since the magnetic islands are thought to contain about 4000 spins, the CoCl_2 system is particularly well suited to a Monte Carlo calculation of the spin states in the magnetic phase diagram. Such a Monte Carlo calculation has been carried out and has been especially helpful in identifying the spin arrangements in the low temperature magnetically ordered phases.

2.6.5 Study of Magnetic Phase Transitions in Acceptor Compounds from Anomalies in the Transport Properties

The strong coupling between graphite layers and Eu layers in the donor compound C_6Eu results in strong spin scattering effects on the graphite conduction π -electrons by the magnetic excitations of the Eu ions. Therefore dramatic changes in the magnetoresistance of C_6Eu are observed as the system undergoes magnetic phase transitions (# 52). Because of the strong interaction, the magnetic phase transitions occur at very high magnetic fields (from several tesla to over 20 tesla) (# 52). In contrast, the acceptor-type magnetic GICs have a much weaker coupling between the intercalate

and the graphite layers because of the much larger separation between the graphite conduction electrons and the magnetic species. Therefore the change in the magnetoresistance due to changes in magnetic ordering is expected to be small and to occur at much lower fields. This is indeed found to be the case.

CoCl₂-GICs are well known as 2D-XY systems with a strong ferromagnetic in-plane nearest neighbor coupling and a relatively weak antiferromagnetic interplane coupling. From magnetic susceptibility and Monte Carlo studies that we have previously carried out (# 58, # 64), stage-1 CoCl₂-GIC samples are known to exhibit three magnetic phases at low temperatures. For zero magnetic field, adjacent planes of ferromagnetically ordered Co²⁺ spins (superspin planes) are antiferromagnetically ordered with respect to each other. At a lower critical field these superspin planes undergo a spin flop transition and the superspins align along easy axes, making angles of 120° with respect to each other. At a somewhat higher field a transition is made to a spin aligned paramagnetic state, whereby all spins are aligned along the externally applied magnetic field. In zero magnetic field two distinct peaks in the magnetic susceptibility are observed, at $T_{c1} \sim 8.3$ K and $T_{c2} \sim 9.7$ K, corresponding to the onset of magnetic order.

The zero-field temperature-dependent resistivity measurements for stage-1 and stage-2 CoCl₂-GICs each show anomalous behavior (# 65, # 73, # 79, # 81, # 83). For the stage 1 compound the anomalous behavior at the magnetic phase transition is large and of opposite sign to what is typically observed in magnetic spin systems. At high temperatures, $T \gg T_c$, the temperature dependence of the resistivity obeys the standard functional form $\rho(T) = A + BT + CT^2$ typical of GICs. Below about 25 K, $\rho(T)$ shows less T dependence than would be expected from the standard functional form, and as T decreases below T_{c2} , a sharp increase in $\rho(T)$ is observed. Spin disorder scattering, characteristic of magnetic systems in the paramagnetic phase, typically result in a lowering of $\rho(T)$ below the magnetic ordering temperature. This effect has been explained in terms of Fermi surface changes associated with a doubling of the magnetic unit cell as antiferromagnetic alignment of the superspin planes is established. Theoretical models for these effects have been developed and they account well for the experimental magnetoresistance measurements.

Interesting behavior is also observed in the stage 1 compound as a function of magnetic field (# 79, # 81, # 83). Below T_{c1} , the resistivity $\rho(H)$ is almost independent of H until H_{c2} is reached corresponding to the alignment of the superspin planes along the magnetic field. Above H_{c2} , $\rho(H)$ is observed to decrease and to saturate at much higher fields. No anomaly in $\rho(H)$ is observed at H_{c1} . The temperature dependence of these phenomena has been studied experimentally and a model has been developed to explain the observed field dependence in the various magnetic phases (# 82).

The behavior of $\rho(T, H)$ for the stage 2 CoCl₂-GIC is qualitatively different from that in stage 1 with regard to both sign and magnitude. As a function of temperature, the stage 2 compound shows a decrease in $\rho(T, 0)$ as T falls below T_{c1} , as expected from the enhanced spin disorder scattering above T_{c1} . The magnitude of the discontinuities in $\rho(T, H)$ at the magnetic phase transitions is much smaller for the stage 2 compound

relative to stage 1, as expected from the much weaker interplanar exchange coupling. Model calculations have been made to account for the relative magnitudes observed for the stage dependence of the magnetoresistance (# 82).

Anomalous behavior has also been observed in the stage 1 MnCl_2 -GICs, qualitatively different from that observed in the CoCl_2 -GICs (# 59).

2.6.6 Magnetic Donor GICs

The only donor magnetic GIC that has been prepared in a form suitable for magnetic measurements is the first stage compound C_6Eu . We have studied the magnetic phase diagram for this compound using high field magnetoresistance techniques, employing the highest fields available with the hybrid magnet at the Francis Bitter National Magnet Laboratory (see § 2.5.3). Monte Carlo spin simulation calculations initially developed to explain the magnetic phases in the CoCl_2 -GIC system have been extended to C_6Eu . These calculations have been useful in identifying a new magnetic phase transition with a canted spin phase. In addition, the calculations have indicated the presence of a 6-fold in-plane symmetry-breaking field (# 52, # 56).

2.6.7 High Field Magnetization of Stage 1 CoCl_2 -GICs

The high field magnetization of stage 1 CoCl_2 -GICs was studied as a function of field up to 18 tesla (# 87). Of particular interest has been the hysteretic behavior that has been observed well above the magnetic phase transition, indicating that there is no remanent magnetization. High field magnetization measurements provide important information on the magnetic parameters for the intercalate layer.

2.7 Superconductivity Studies in Graphite Intercalation Compounds

2.7.1 Superconductivity in KHg -GICs

We have been studying the relation between the synthesis conditions, the in-plane structure and the superconducting transition temperature T_c and width ΔT_c (# 15, # 41). Of particular interest is the wide range of superconducting transition temperatures that have been reported ($0.72 < T_c < 1.55$ K) for the stage 1 compound, and the observation that T_c for the stage 1 compound is lower than that for the stage 2 compound, though heat capacity measurements indicate a higher density of states for the stage 1 compound.

In this work, the superconductivity in ternary GICs has been compared with the superconductivity in anisotropic layered compounds and MBE superlattices (# 4, # 54) and to anisotropic high T_c superconductors (# 80).

2.7.2 Superconductivity in Hydrogenated KHg -GICs

When stage 1 KHg -GICs are doped with hydrogen, the transition temperature was found to rise to the maximum observed value of $T_c \approx 1.55$ K, independent of the transi-

tion temperature prior to the hydrogenation (# 26, # 30, # 84). In the hydrogenation process, the transition width ΔT_c is also greatly narrowed. The physical basis for this stabilization of the superconducting transition by the addition of hydrogen is under investigation using high resolution x-ray and neutron scattering techniques (# 85) to look for structural effects relating to this stabilization of the superconducting phase transition.

2.7.3 Superconductivity in Cs-Bi-GICs

Following up on a report that the Cs-Bi-GICs were superconducting with a T_c value much above that of KHg-GICs ($T_c = 1.9\text{K}$), we prepared Cs-Bi-GIC samples and measured the low temperature susceptibility (# 63) looking for a Meissner effect, but none was found down to 1K.

2.7.4 Surface Phenomena

A visit by Dr. Michel Laguës from Paris stimulated investigation of whether or not there is intercalant depletion in the surface layer of acceptor GICs and intercalant enhancement for donor GICs (# 91). In collaboration with Laguës, XPS and Auger measurements have been carried out at MIT in the acceptor CoCl_2 -GICs and CuCl_2 -GICs (# 91). The results support the intercalate depletion for these acceptor compounds. Previous work on the donor Cs-GICs indicate intercalate enhancement (# 76).

2.8 Review Articles and Plenary Invited Talks

A short review article has been prepared for the *Materials Research Encyclopedia*, and has been published by Pergamon Press (# 1). An invited plenary paper for the European Physical Society on recent advances in research on GICs was presented (# 29). An article for *Physics Today* has been prepared for publication based on the retiring APS presidential address in which research on GICs was discussed (# 31). In response to a request to highlight the research opportunities in graphite intercalation compounds at the Fourth International Conference on Intercalated Graphite at Tsukuba, Japan (1985), a review article has been prepared (# 37). In connection with the book "Intercalation in Layered Materials" (# 67), review articles were prepared on microscopic studies of GICs (# 68), superlattices and intercalation compounds (# 75), electron spectroscopies in GICs (# 76), magnetism in GICs (# 71), and superconductivity in GICs (# 70).

A review article on 2D magnetism was prepared for a magnetism workshop (# 58), and a book was prepared from extended abstracts for the 1986 MRS meeting on Graphite Intercalation Compounds (# 77). A review article on intercalation into layered materials was prepared for the Bulletin of the MRS (# 78). Overview comments were prepared for the closing of the 4th International Conference on Graphite Intercalation Compounds (# 90).

3 Reports and Publications

3.1 Publications

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3. "Raman Microprobe Studies of the Structure of SbCl_5 Graphite Intercalation Compounds", L.E. McNeil, J. Steinbeck, L. Salamanca-Riba and G. Dresselhaus, *Bull. APS* **29**, 253 (1984).
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7. "Intercalation of Ion Implanted Graphite", H. Menjo, B.S. Elman, G. Braunstein, and M.S. Dresselhaus, *J. de Chimie Physique* **81**, 835 (1984).
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15. "Structural Order, Stoichiometry and Superconductivity in $\text{KHg}_x - \text{GIC}$ ", G. Roth, N.C. Yeh, A. Chaiken, G. Dresselhaus, and P. Tedrow, *Extended Abstracts of the Symposium on Intercalated Graphite at the Materials Research Society Meeting*, edited by P.C. Eklund, M.S. Dresselhaus and G. Dresselhaus, Boston (1984), p. 149.
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19. "High Resolution Electron Microscopy Studies of Potassium-Hydrogen Intercalated Graphite", L. Salamanca-Riba, N.C. Yeh, T. Enoki, M.S. Dresselhaus, and M. Endo, *Extended Abstracts of the Symposium on Intercalated*

Graphite at the Materials Research Society Meeting, edited by P.C. Eklund, M.S. Dresselhaus and G. Dresselhaus, Boston (1984), p. 249.

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26. "The Effect of Hydrogen Doping on the Superconducting Transition Temperature of KHg -GIC", G. Roth, A. Chaiken, T. Enoki, N.C. Yeh, G. Dresselhaus, and P. Tedrow, *Extended Abstracts of the 17th Biennial Conference on Carbon*, June 16-21, 1985, University of Kentucky, p. 63.
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71. "Magnetism in Graphite Intercalation Compounds", G. Dresselhaus and M.S. Dresselhaus, *Intercalation in Layered Materials*, ed. M.S. Dresselhaus, (Plenum Press, New York, 1987), p. 407.
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80. "Low temperature H_{c2} measurements in C_4KHg_x ", A. Chaiken and M. S. Dresselhaus, In *Extended Abstracts of the 18th Biennial Conference on Carbon*, page 133, (1987), July 19-24, 1987, Worcester Polytechnic Institute.
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88. "C-axis conduction in graphite intercalation compounds", K. Sugihara, *Synthetic Metals*, **23**, 359, (1987).
89. "Quasi-Two-Dimensional Phase Transitions in Graphite Intercalation Compounds", G. Dresselhaus, M. S. Dresselhaus, and J. T. Nicholls, Volume xx of *Springer Proceedings in Physics*, Springer-Verlag, Berlin, (1988), Proceedings of an International Workshop, Los Alamos, New Mexico.
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91. "Intercalant Depth Profile in Acceptor-type Metal-Chloride Graphite Intercalation Compounds", M. Laguës, X. Hao and M. S. Dresselhaus, *Phys. Rev.*, **B37**, (1988).

3.2 Advanced Degrees and Honors

- M.S. Dresselhaus
Appointed Institute Professor at MIT, December, 1985.
- M.S. Dresselhaus
awarded Killian Prize for 1986-1987 (April 1986).
- M.S. Dresselhaus
named Phi Beta Kappa Lecturer, 1986-1987.
- M.S. Dresselhaus
elected to Council, National Academy of Sciences, March 1987.
- M.S. Dresselhaus
elected Chairman, Engineering Section, National Academy of Sciences, February 1987.
- K.Y. Szeto, Ph.D., Physics, January 1985.
"Two-Dimensional XY Models and Its Application to Graphite Intercalation Compounds",

- L. Salamanca-Riba, Ph.D., Physics, July 1985.
"Structural Studies of Graphite Intercalation Compounds and Ion Implanted Graphite".
- S.T. Chen, Ph.D., Department of Physics, November 1985.
"Magnetic Properties of Graphite Intercalation Compounds".
- Y.C. Yeh, Ph.D., Department of Physics, January 1988.
"Electronic and Magnetic Properties of Graphite Intercalation Compounds".
- A. Antonious, M.S., Department of Chemistry, February, 1987.
"Fundamental Properties of the Oleophilic Graphite",
- H. Menjo, M.S., Department of Materials Science and Engineering, June, 1985.
"Ion Implantation Enhanced Intercalation in Graphite",

4 Personnel Involved with Research Program

- Mildred Dresselhaus - Principal Investigator.
Responsible for the research and the direction of all aspects of the program.
- Gene Dresselhaus - Co-principal Investigator.
Responsible together with the principal investigator for the research and the direction of all aspects of the program.
- G. Doll - Postdoctoral Associate.
Responsible for infrared and Raman measurements of high T_c superconductors.
- Michel Laguës - Visiting Scientist.
Spent 6 months with our research group (May-November, 1986), introducing us to surface science measurements on graphite intercalation compounds.
- I. Ohana - Postdoctoral Associate.
Responsible for the scanning tunneling microscopy program and for the study of the Raman spectra in high T_c superconductors.
- Gerhard Roth - Postdoctoral Fellow.
Responsible for high resolution x-ray measurements and for the synthesis and measurements of superconducting properties of graphite intercalation compounds. (Left June 1985 to take an R & D position at Bruker Industries, Karlsruhe, West Germany).
- Ko Sugihara - Research Staff.
Responsible for modeling transport properties of GICs and of scattering processes in magnetic intercalation compounds.

- Alla Antonious - Research Assistant.
Worked briefly in setting up system for infrared spectroscopy studies in graphite intercalation compounds. Completed MS thesis in February 1987 and left MIT.
- Alison Chaiken - Research Assistant and IBM Graduate Fellowship Student.
Responsible for superconductivity studies in intercalated graphite, and synthesis, characterization and properties measurements on these compounds. Also studies relation of anisotropic GIC superconductors to high T_c superconductors.
- Shyng-Tsong Chen - Research Assistant and Graduate Fellowship Student.
Responsible for the synthesis of magnetic intercalation compounds, for high precision measurements of the magnetic susceptibility and magnetization of these compounds as a function of temperature and external magnetic fields. Is also responsible for modeling spin ordering using Monte Carlo techniques. Completed Ph.D. Thesis in November 1985.
- Chi Chung Chin - Research Assistant.
Responsible for microwave studies in high T_c superconductors.
- Cindy Hao - Research Assistant.
Worked with Michel Lagués on surface science measurements on graphite intercalation compounds while he was at MIT. Now working on scanning tunneling microscopy in another research group.
- H. Jiménez-González, Fellowship Student.
Worked briefly on laboratory work to determine whether oleophilic graphite flakes can be used to synthesize magnetic graphite intercalation compounds that are difficult to intercalate into HOPG or kish graphite host materials. He switched to another project in 1985.
- A. Kazeroonian - Research Assistant.
Responsible for studies of structural phase transitions in graphite intercalation compounds exhibiting superconductivity. Working on infrared spectroscopy of high T_c superconductors.
- Maria Kudisch - Undergraduate Student.
Assisted with synthesis of KHg-GICs and superconductivity measurements. Completed B.S. Thesis in May, 1985.
- Hiroshi Menjo - Fellowship Student.
Responsible for synthesis and measurement of the Na-GICs using ion implantation to enhance the intercalation process. Completed M.S. Thesis in May, 1985.
- J. Nicholls - Research Assistant.
Responsible for low dimensional susceptibility and magnetization studies of magnetic graphite intercalation compounds and related Monte Carlo model calculations.

- Lourdes Salamanca-Riba – Research Assistant.
Responsible for structural studies of intercalated graphite using x-ray diffraction, real space imaging and lattice fringing, with particular emphasis on phase transitions. Completed Ph.D. Thesis in July, 1985.
- James Speck – Research Assistant.
(NSF Fellow for academic years 1984–1987). Responsible for structural studies of intercalated graphite using x-ray diffraction, electron diffraction, real space imaging and lattice fringing, with particular emphasis on the orientational locking phenomenon.
- Kwok-Yip Szeto – Research Assistant and Graduate Fellowship Student.
Responsible for extension of two-dimensional xy model to calculate susceptibility for magnetic GIC including finite domain size effects, magnetic phase diagrams and spin flop transitions. Completed Ph.D. Thesis in January, 1985.
- N.C. Yeh – Research Assistant.
Responsible for transport studies of low dimensional magnetism in magnetic graphite intercalation compounds. Completed Ph.D. in January, 1988.

4.1 Coupling Activities – Seminars and Invited Conference Papers

The MIT group is strongly coupled to international activities on graphite intercalation compounds. Below are listed titles of seminars, invited talks and symposia given over the three year October 1, 1984 to September 30, 1987 period relevant to the work supported under this contract. Significant coupling activities are also listed.

- October 10, 1984, University of Massachusetts, Amherst MA, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- November 21, 1984, McMaster University, Hamilton, Ontario, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- January 7, 1985, Solid State Physics Division Seminar, Oak Ridge National Laboratory, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- January 16, 1985, University of West Virginia, University Lecture, "Science Education for this Decade", (MSD).
- January 17, 1985, University of Toronto, Toronto, Canada, Physics Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- January 23, 1985, University of California, Berkeley, California, Physics Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).

- January 31, 1985, Stanford University, Stanford, CA, Materials Science Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- February 1, 1985, University of California, Berkeley, Quantum Electronics Seminar, "New Materials for Applications in Quantum Electronics and Superconductivity", (MSD).
- March 20, 1985, European Physical Society, Invited Plenary Lecture, Berlin, West Germany, "Layered Crystals and Intercalated Compounds", (MSD).
- March 26, 1985, American Physical Society, March Meeting, Baltimore, MD, "Perspectives on the Presidency of the American Physical Society", (MSD).
- April 12, 1985, IBM Research Laboratory, San Jose CA, Laboratory Seminar, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- April 25, 1985, AFOSR, Bolling Air Force Base, Washington, DC, "Opportunities and New Directions In Graphite Intercalation Compounds", (MSD).
- May 17, 1985, Xerox Research Laboratory, Palo Alto, CA, Laboratory Seminar, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- May 18, 1985, University of California, Berkeley, CA, School of Engineering, Commencement Address, "The Challenge of Youth", (MSD).
- June 19, 1985, Invited talk, CRDC Scientific Conference on Obscuration and Aerosol Research, June 17-21, 1985, Aberdeen Proving Grounds, MD, "Intercalated Fibers Derived from Benzene", (MSD).
- October, 28, 1985, National Academy, Washington DC, "Basic Research Supported by Mission Agencies", (MSD).
- November 18, 1985, University of Virginia, Materials Science Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- January 6, 1986, International Workshop on Low Dimensional Magnetism, Taxco, Mexico, Invited Talk, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- January 15, 1986, University of Minnesota, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- January 30, 1986, Rutgers University, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- March 4, 1986, Union Carbide Research Center, Parma Ohio, Seminar, "Overview of Carbon-related Research in the Dresselhaus Group", (MSD).

- May 15, 1986, Texas Instruments Central Research Laboratory, Dallas, Texas, "New Advances in Intercalation into Layered Materials", (MSD).
- May 23, 1986, Materials Research Society, Inauguration of New York Section, Keynote Speech on "New Materials Synthesis by Intercalation and Implantation", (MSD).
- July 5-15, 1986, NATO Summer School at Erice, Sicily on "Intercalation in Layered Materials". MSD was the Director of the Summer School, and the Editor of the NATO Proceedings published by Plenum Press (# 67). In connection with the summer school, several review articles were prepared and presented orally:
 - "Electron Spectroscopies", (GD).
 - "Superconductivity in Graphite Intercalation Compounds", (GD).
 - "Magnetism in Graphite Intercalation Compounds", (GD).
 - "Superlattices and Intercalation Compounds", (MSD).
 - "Microscopic Studies of Intercalated Graphite", (MSD).
- July 21, 1986, DARPA Workshop on Magnetism and Magnetic Materials, San Diego, CA, "Low Dimensional Magnetism in Graphite Intercalation Compounds", (GD).
- September 19, 1986, Solid State Seminar, Purdue University, "Magnetic Phase Transitions in Graphite Intercalation Compounds", (GD).
- October 21, 1986, Meeting with Dr. L. Shepard and Dr. J. Perkins of Army Materials Research Center to discuss intercalation of specific transition metals into graphite, (MSD and GD).
- November 25, 1986, Materials Science Colloquium, Carnegie Mellon University, "Phase Transitions in Graphite Intercalation Compounds", (MSD).
- December 3-5, 1986, Organized Materials Research Society Symposium on "Graphite Intercalation Compounds", (MSD and GD).
- December 6-11, 1986, Visits for several days by several distinguished workers on intercalation compounds: Dr. M. Laguës, Professor M. Matsuura, Dr. H. Miyazaki, Dr. T. Takahashi, Dr. T. Enoki, Dr. M. Endo, (MSD and GD).
- December 10, 1986, Materials Science Distinguished Lecture Series, University of Connecticut (Storrs), "Phase Transitions in Graphite Intercalation Compounds", (MSD).
- December 22, 1986, Meeting with Dr. F. Huffman of Thermoelectron Corporation regarding possible applications of intercalation compounds, (MSD).

- January - mid March, 1987, Phi Beta Kappa Lectures on 8 campuses, including lectures on Frontiers of Solid State Physics, New Materials by Intercalation and Implantation, Phase Transitions in Intercalation Compounds, Superlattices, (MSD).
- January 23, 1986, Physics Colloquium, University of Wisconsin, "Phase Transitions in Graphite Intercalation Compounds", (MSD).
- January 29, 1986, Physics Colloquium, University of South Carolina, "Phase Transitions in Graphite Intercalation Compounds", (MSD).
- March 16-21, 1987, American Physical Society March Meeting, Several papers were presented and we interacted with many researchers, (MSD and GD).
- March 24, 1987, Physics Colloquium, SUNY Binghamton, "Phase Transitions in Intercalation Compounds", (MSD).
- April 1, 1987, Killian Lecture, MIT, "Adventures in Carbon Research", (MSD).
- April 8, 1987, Killian Lecture, MIT, "New Materials and New Science by Intercalation", (MSD).
- May 2, 1987, invited lecture at Los Alamos workshop on "Quasi-Two-Dimensional Phase Transitions in Graphite Intercalation Compounds", (GD).
- May 25, 1987, invited lecture at 4th International Symposium on Graphite Intercalation Compounds, Jerusalem on "Ion implantation in graphite as a precursor for intercalation", (MSD).
- May 25, 1987, conference summary lecture at 4th International Symposium on Graphite Intercalation Compounds, Jerusalem on "Overview comments", (MSD).
- May 25, 1987, lecture at 4th International Symposium on Graphite Intercalation Compounds, Jerusalem on "High field magnetization of CoCl₂-GICs", (GD).
- July 20, 1987, lecture at the 18th Biennial Conference on Carbon, Worcester Polytechnic Institute on "Transport Properties in CoCl₂ Graphite Intercalation Compounds", (GD).
- July 20, 1987, lecture at the 18th Biennial Conference on Carbon, Worcester Polytechnic Institute on "Low Temperature H_{c2} measurements in C₄KHg₂", (MSD).

5 New Discoveries, Patents or Inventions

None.